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INFLUENCE OF 5f ELECTRONS ON STRUCTURE AND BONDING IN THE ACTINIDE-HYDROGEN INTERMETALLICS*

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The physicochemical properties of the early actinide (through Pu) hydrides present a fascinating electronic picture that is unique in the periodic table. Complex phases form for the Th + H and U + H systems that are found with no other metals. In the Pa + H system, simple body-centered cubic, C15 Laves and A15 phases can form, dependent on temperature and composition. The phase transformations appear to be magnetically-driven, as a result of the deccupling of the metallic 5f electron bonding that occurs during hydriding; the C15 phases contain two kinds of Pa atoms--the one sublattice being still fully f-bonded and the other magnetic. This is a unique situation in solid state physics which defies a valence description. A similar situation obtains for A15 β - UH_3 structure. It can be shown that the parent metals themselves exhibit electronegativities not unlike those of the mid-3d transition metals (e.g , Fe) because the valence electrons are tied up in metallic bonding. However, under the driving force for hydriding, the lattices can open up, decoupling the f-bonding and inducing magnetism. The systems then aggressively form very stable hydrides typical of highly-electro-positive metals.

Beyond uranium the trivalent metallic state is favored and rare-earth-like hydrides are found for Np + H and Pu + H. Nevertheless, the solid-state and transport properties are markedly different than for the rare-earth hydrides, showing that the latent influence of the 5f electrons is still strong.

*Subject category: Early actinide-hydrogen intermetallics.

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Introduction

The general behavior of metallic (i.e., electrically conducting) hydrides has been discussed by Ward.[1] Briefly, the great majority of these metal-hydrogen intermetallics is made up of hydrides of trivalent electropositive metals. No mono or divalent metallic hydrides are known, only a handful of tetravalent (Ti, Zr, Hf, Th) and still fewer pentavalent (V, Nb, Ta) hydrides are found; the higher metallic valencies go with lower electronegatives and at the same time smaller lattices (of the metals) with high cohensive energies, and the resultant hydrides are of low composition and not particularly stable.

The behavior of the trivalent rare-earth hydrides plus Y and Sc is relatively well-understood, or at least thoroughly studied. These metals remain trivalent while first forming a dihydride, MH_2, whose electrical conductivity is higher than that of the parent metal due to the "spare" electron sitting in the conduction band. Upon approaching the trihydride solid solutions are formed, with several possible intermediate phases before a final hexagonal modification, for the heavier (Sm and beyond) metals. Various stages of semi-metal/semiconductor/insulator behavior are seen in the MH_2 - MH_3 regime. This sort of chemistry is first seen in the actinides for the metals neptunium and beyond, but the solid state properties are markedly different, as will be noted below.

In the tetravalent metals Ti, Zr and Hf several intermediate (i.e., bcc, fcc) phases are seen with increased hydrogen content, up to a limiting MH_2 composition, for which a face-centered tetragonal structure is found for these metals. The electrical resistivity also drops in approaching the composition MH_2, reflecting an increasing metallic character.

THE EARLY ACTINIDE-HYDROGEN SYSTEMS

The Thorium-Hydrogen System

Face-centered tetragonal ThH_2 appears to be the proper homolog for the Ti-, Zr- and Hf- + hydrogen systems, until the solid state properties are looked at more closely. The phase forms easily, without intermediate complexities, and the trends in lattice constants and heats of formation change abruptly, as shown in Table 1.

TABLE 1

Hydrides of Tetravalent Metals

		TiH_2	ZrH_2	HF_2	ThH_2
Lattice constant (fct)	a_o =	4.528	4.881	4.919	5.735
	c_o =	4.279	4.449	4.363	4.971
Metal-hydrogen distance (Å)		1.92	2.11	2.05	2.38
ΔH_f° (298), kcal/mol		29.9	38.9	44.0	35.0

As can be seen, there is a startling increase in lattice constant and a totally non-characteristic (for a tetravalent metal) metal-hydrogen distance for ZrH_2; concomitantly there is a large drop in the heat of formation, interrupting a rising trend for the other three metals.

Looked at in another way, the lattice is simply huge, and raising the hydrogen pressure leads to another well-defined phase Th_4H_{15} (Th 3.75), i.e., a nearly tetra-hydride with a complex bcc structure containing 16 thorium atoms per unit cell. The Th-atoms form 12 almost perfect tetrahedra with common vertices but no common sides. Within each tetrahedron lies one H-atom, and thus there are 12 such atoms in the unit cell, with 48 "type II" hydrogen atoms lying just above the face of these tetrahedra. Structures of the two thorium hyrides are shown in Figure 1.

Metal hydrogen distances in the Th_4H_{15} structure vary from 2.27 to 2.46Å. The large Th-Th distance (larger than the oxide) implies little residual metallic bonding, yet this phase is a superconductor.[2,3] Much has been written about this uncommon occurrence, and the physicochemical and solid-state properties of the Th + H system have been reviewed by Ward.[4]

The electronic behavior of Th_4H_{15} has been discussed in terms of a significant contribution from the tail of the 5f band, which lies less than 1eV above the Fermi level for thorium metal (but should lie considerably higher for the hydrides). Cluster calculations by Winter and Ries[5] indicate considerable 5f character in the density-of-states, and Dietrich et al.[6] proposed an f-band mechanism for the high positive pressure effect. Miller et al.[7] found a relatively-large electronic specific heat, which is however, at odds with the photoemission studies of Weaver et al.,[8] showing a narrow conduction d-band near the Fermi level and a rather low density-of-states at the Fermi level. Clearly, more work needs to be done on this fascinating hydride.

The Protactinium - Hydrogen System

The first broad-band 5f-electron appears at protactinium, and there results a situation unique in the periodic table--a C15 Laves phase AB_2-type structure from about $PaH_{1.33}$ $PaH_{1.68}$, in which the protactinium atoms assume both metal positions A and B, in the two sublattices; the phase forms at temperatures above 500 K. This structure is shown in Figure 2. The large open circles indicate the A-lattice of widely-spaced Pa-atoms, each surrounded by four other type A atoms at a metal-metal distance of 3.997Å, large enough, according to the concepts embodied in the "Hill Plots"[9] to permit localized 5f electrons, i.e., magnetism. By contrast, the type-B sublattice, shown with the smaller shaded circles, forms as a closely-spaced 6-coordinated system with corner-shared B_4 tetrahedra and with metal-metal distances of only 3.264Å, scarcely larger than Pa metal (3.215Å). The area delineated by dotted lines in Fig. 2 is essentially the (110) body-diagonal plane of fct Pa-metal, virtually unchanged by the hydriding process.

Additionally, the A/B radius ratio is precisely the ideal value of 1.225 for a perfect C15 structure with only A-A and B-B contacts; however, since the shortest A-A distance is much too large for a believable Pa-metal radius, this sublattice must be formed by metal-hydrogen bands, giving a "pseudo-radius" of proper value. The B-sublattice is then metallic and still highly f-bonded, with smaller Pa-atoms, whereas the A-atoms should be larger.

Ward et al.[10] have discussed the physicochemical and thermodynamic properties of the Pa + H system in detail, and showed that the C15 phase is magnetic with magnetic moment U_{eff} at 298K = 0.84 μB; clearly, the magnetism must lie at the type-A atoms, the metallic character with the type-B sublattice. At temperatures below about 500K a simple bcc phase forms, isostructural with α - UH_3. The phase again first appears at $PaH_{1.3}$, and retains the structure to PaH_{3-x}($x < 0.1$). Remarkable is the observation that the lattice is fully established at H/Pa = 1.3, with 57% of the anion sites vacant, and there is no further expansion of the molar volume up to the full composition. The simple bcc structure can be viewed as a removal of the tetragonal distortion of the fct metal lattice, followed by an expansion due to the driving force for hydriding; the metal atoms must move grudgingly at the lower temperatures (whereas the hydrogen can move freely). Ward et al.[10] argue, on the basis of an observed magnetic movement and the surprising stabilization of the phase at such a low composition, that the localization of the 5f electron in the formation of the bcc phase provides the best means to accommodate the entering hydrogen at these low temperatures.

London[11] has provided evidence that the β - UH_3 structure must always nucleate on α - UH_3 microcrystallites. If this mechanism also applies to the Pa + H system, the puzzlingly-consistent lower phase boundary of H/Pa = 1.3 for both the C15 and the bcc phases can also be understood. Then the more complex (C15) phase would always nucleate on α-PaH_3 pre-cursor microcrystallites at the higher temperatures; the C15 phase, though more complex, is the lower energy state, the bcc phase is in reality metastable, and the system transforms to the C15 structure when metal atom mobility becomes appreciable.

The Higher Hydrides: β - PaH_3 and β - UH_3

At temperatures above 500K and H/Pa > ~ 2.0, the system again opts for a new phase, this time the almost equally complex A15 β - UH_3 structure. In contrast to uranium, the hydride exists over a stoichiometry range: β - PaH_{3-x} ($0.1 < X < 1.0$). The metals Pa and U then share this peculiar structural modification, unique among hydrides in the entire periodic table. For an A15 structure to form these must be two kinds of metal atoms present, so again there are two

sublattices, as shown in Fig. 3. The shaded larger circles lie in a bcc lattice with widely-spaced and presumably magnetic metal atoms, whereas the open circles show infinite chains of closely-spaced atoms, two in each cube face; these chains closely-resemble the rows of type B atoms in the C15 structure (Fig. 2). The metal-metal distance in the face chains is only 3.31Å; Ward et al.[12] have shown through relativistic Wigner-Seitz band calculations that there should be major f-f overlap of the 5f (t_{1u}) wave functions for this distance, implying strong metallic bonding in the type-II sublattice of face chains, as also verified by the electrical resistivity measurements. Switendick[13] has calculated electronic energy bands for both the α and β hydrides. Evidence was found for considerable uranium-f/hydrogen-s bonding, which is actually favored by both structures. Both localized (magnetic) and itinerant f-characters were identified, the latter as large as two electrons/U-atom for the linear chain (type II) atoms in the A15 structure; however, potentials constructed for the two kinds of uranium differed by only 0.01 Rydberg. XPS studies[12] on the β-deuteride showed well-defined core-level 4f spectra without satellites with no evidence of more than one valence state; energies indicate a metallic valence somewhere between U^{+4} (f^2) and the metal.

Then the type-I sublattice seems like the most likely candidate for the locations of the magnetic moments, but there is as yet no solid evidence for this. The measured paramagnetic moment for β - PaH_3 is 0.96 μ_β, whereas measured values for β - UH_3 range from 2.44 - 2.79 μβ (far below the expected value for a localized U^{+3} or U^{+4} state). Conversely, assigning the full magnetism to the type I sublattice (I/II ratio = 1:3) would result in too high a value. New neutron diffraction and neutron inelastic scattering studies[14] will hopefully finally resolve this question.

It is instructive to consider both the α- and β-hydrides in terms of cohesive energies holding the lattices together. In the α-hydride each uranium atom is surrounded by an icosahedron of hydrogen atoms, i.e., this lattice is held together primarily by metal-hydrogen bonds, which is typical of most hydrides. In the β-hydride, this same set of

icosahedra now surrounds only the metal atoms in the bcc type I sublattice (now considerably expanded) and the type II sublattice then retains a metal-metal distance not unlike that of the metal. In a sense, the type II sublattice is "inserted" into the positions formely occupied by hydrogens in the α-hydride. In the lattice there are then two radii: the 1.67Å contacts of the type II sublattice, and the 2.03Å contacts of the type I sublattice--actually then a "pseudo" M-H radius; the I-II distance also preserves this relationship, i.e., 1.67 + 2.03.

In the preceding discussions, the concept of metal valence has been avoided; it is very different to reconcile f-electron overlap with the normal s, p, d valence picture. Rather, the concept of at least partially-localized f-electrons (larger atoms), and bonding and metallic f-electrons (smaller atoms) has been emphasized. The simplest response of early actinide compounds to a chemical driving force is to either localize or delocalize the f electrons, thus turning off the f-bonding; the result is often unusual structures and complex phase transformations.

The Systems Np + H and Beyond

As noted in the introduction, there is a sudden change at neptunium to rare-earth-like chemistry. Since there is still a maximum of f character at Np, the result is probably due to the solid preference for trivalency for this and the following metals. The metal-hydrogen distance is already at a minimum (2.32Å) for trivalent hydrides at NpH_2, and there is no evidence for magnetism or magnetic ordering, though the Np-Np distance is large and the 5f electrons should be well-localized; however, the Np-5f/H-1s interactions should not be ignored.

The solid state properties of the Pu + H system are interesting and complex, and are discussed by Willis et al.[15] These properties are markedly-different than for the rare-earth hydrides, and one would then expect another radical change beginning at americium or perhaps curium, where the 5f's truly become core-like. Unfortunately, measurements revealing this have yet to be done.

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Figure Captions

1.a. Sketch of the ThH_2 structure; the small bct unit cells can be combined in groups of four to form the larger unit cell (outlined by heavy dashed lines) designated as fct. Note the parallel chains of hydrogens (shaded atoms), leaving the front faces of either unit cell as large open channels.

1.b. Section of the Th_4H_{15} structure, showing typical groups of tetrahedra, each enclosing a type I (black) hydrogen. Shown also are some (not all) type II hydrogens, each in the center but slightly out from the plane of a tetrahedral face.

2. Sketch of the unit cell for the C15 Laves-type protactinium hydride. Type A magnetic atoms are shown as larger open circles, type B f-bonded smaller metallic atoms are shown shaded; hydrogens are not shown.

3. Sketch of the A15 β - UH_3 (β - PaH_3) structure. Large U_I atoms (shaded) form the bcc sublattice. Smaller U_{II} atoms (open circles) form the metallic, f-bonded face-chains. Small shaded atoms show hydrogen locations. Also shown are two representative I_1 II_3 tetrahedra.

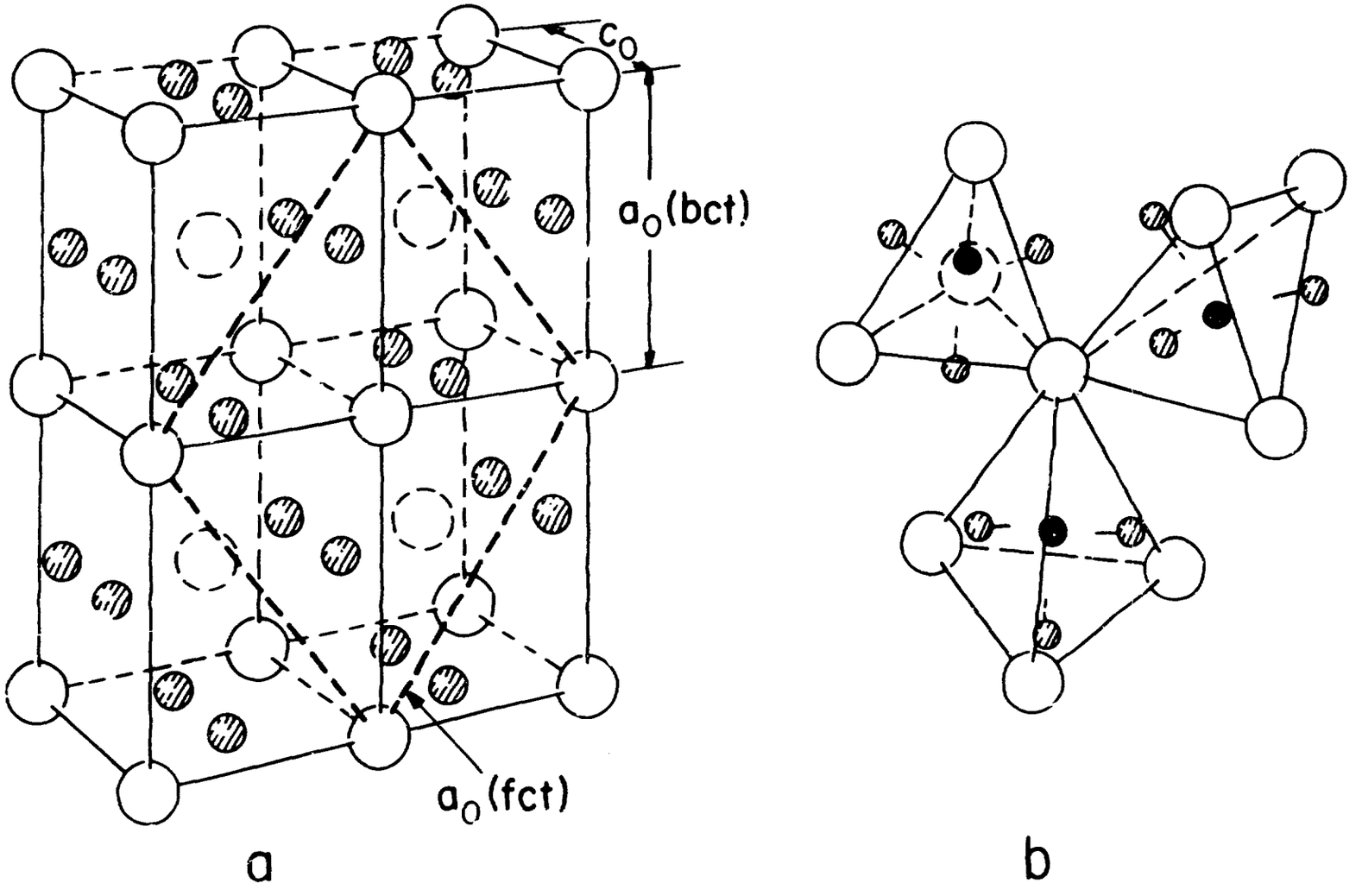

FIGURE 1.

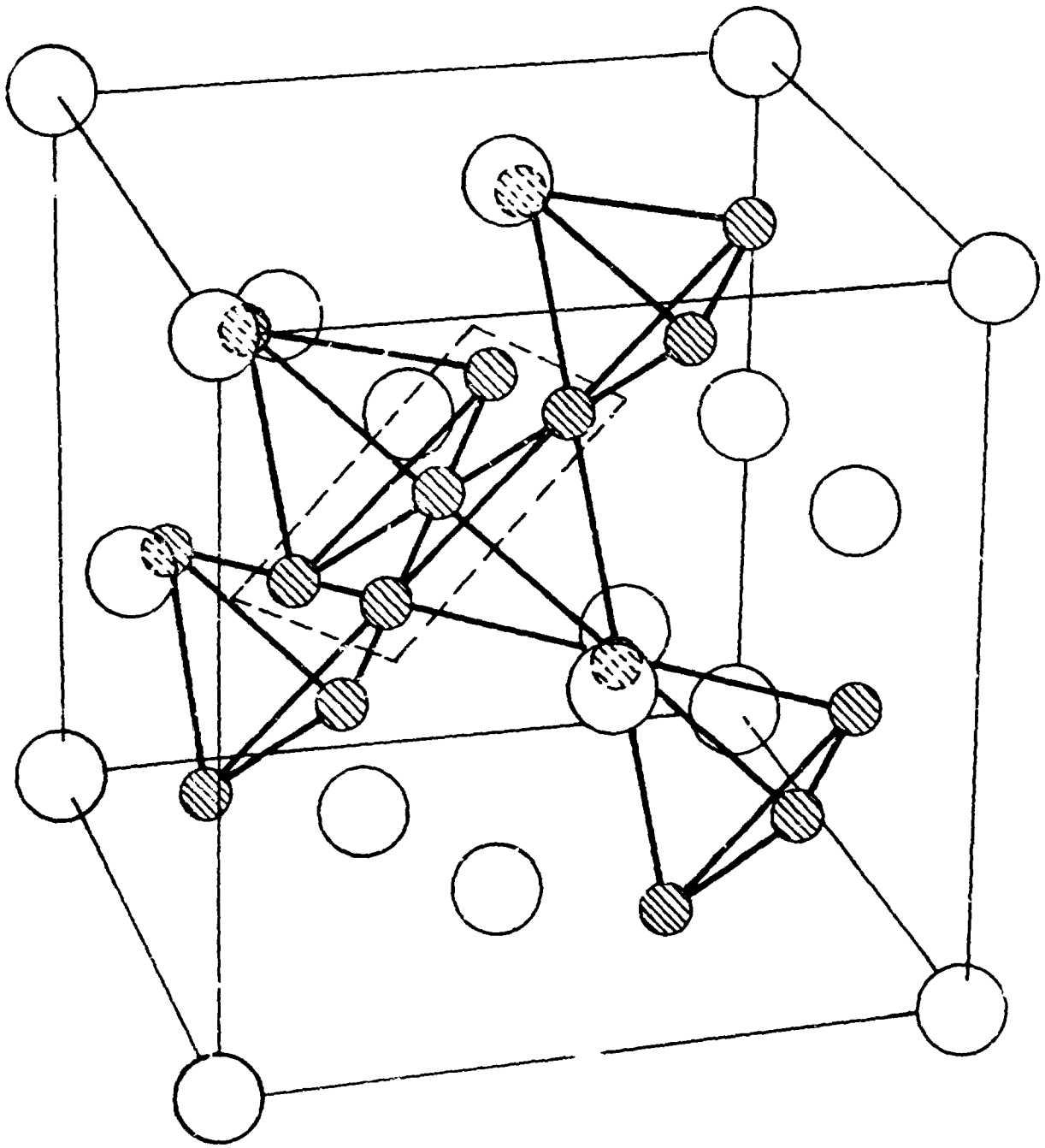

Figure 2.

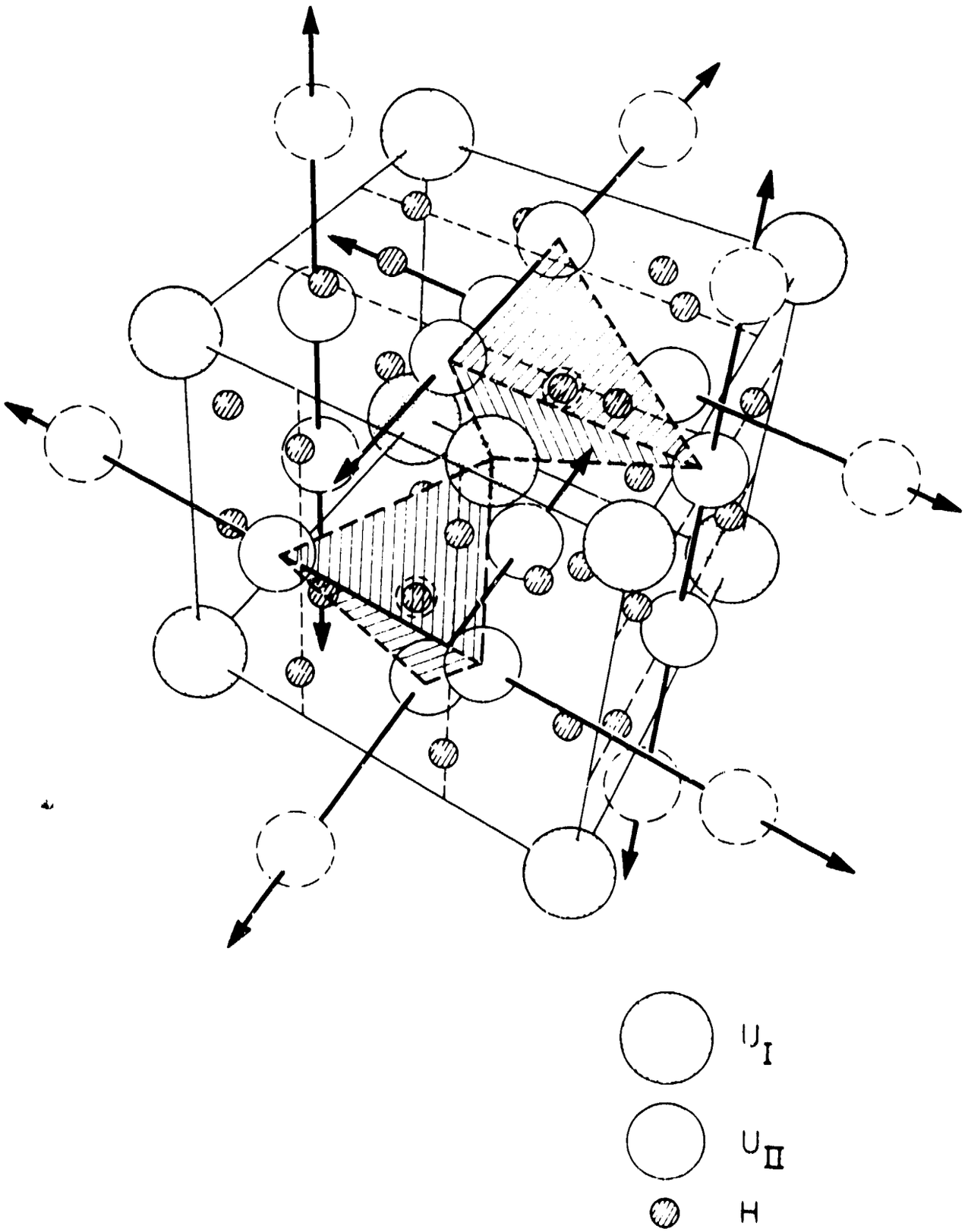

Figure 3.